PATENT SPECIFICATION

(11) 1 284 814

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NO DRAWINGS

(21) Application No. 34367/70 (22) Filed 15 July 1970
(31) Convention Application No. 842 698 (32) Filed 17 July 1969 in
(33) United States of America (US)
(45) Complete Specification published 9 Aug. 1972
(51) International Classification A23D 5/00
(52) Index at acceptance
C5C 9B4 9B9A 9B9B 9B9C1 9B9CX 9B9D 9C2 9E3 9EX

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(54) EDIBLE OIL COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to edible oil compositions, particularly to such compositions comprising a liquid glyceride base oil and a hypocholesterolemic agent.

As used herein, the term "hypocholesterolemic" means reducing the cholesterol level in the blood of warm-blooded animals or inhibiting or reducing the buildup of cholesterol in the blood.

The addition of hypocholesterolemic additives, including plant sterols, to oils is known (See U.S. Patent 3,085,939; U.S. Patent 3,203,862; Canadian Patent 567,202; and Peterson et al. *J. of Nutrition 50,* 191—201 [1953]). However, plant sterols, that is free and unesterified sterols, must be added to the oils in amounts usually less than 0.5% by weight if the oils are to remain clear at refrigerator temperatures or if the added sterol is not to precipitate from the oil in the presence of water; the use of these very low amounts of added sterol do not provide significant hypocholesterolemic activity.

The present invention provides an edible oil composition comprising a liquid glyceride base oil and a plant sterol monocarboxylic acid ester in which the monocarboxylic acid moiety has from 1 to 12 carbon atoms if the carboxylic acid is saturated and up to 24 carbon atoms if the carboxylic acid is unsaturated, the acid plant sterol ester being present in an amount of from 0.5% to 10% (free sterol equivalent) by weight of the composition, provided that the said plant sterol ester is present in an amount such that it is substantially completely soluble in the base oil at 40°F.

The percentages of plant sterol monocarboxylic acid ester herein are calculated as if an equivalent amount of free sterol were present. This is indicated by the use of the expression "(free sterol equivalent)" after the recited percentages.

The plant sterol ester is added to a clear liquid base oil in such an amount as to provide a commercially acceptable dietary cooking and salad oil which remains clear even at refrigerator temperature (40°F for the purposes of the Specification). Generally, the sterol ester will not precipitate from the oil in the presence of water, for example, when a vinegar and oil emulsion is prepared. Thus, the ester may be added to the oil in an effective amount without adversely affecting the appearance of the oil.

The plant sterol monocarboxylic acid esters added as hypocholesterodemic agents have their sterol moieties derived from any free (that is, unesterified) plant sterol. For example, the sterol moieties can be derived from free plant sterols such as, for example, α-sitosterol, β-sitosterol, stigmasterol, ergosterol, or campesterol. The sterol moieties can also be derived from mixtures of these free plant sterols such as soy sterols.

As used herein, the term "plant sterol" includes all non-animal sterols, that is, not only phytosterols (plant sterols characteristic of higher plants) but also mycosterols (plant sterols from lower plants). For a more complete description of plant sterols see Deuel, Jr., Harry J., *The Lipids Vol. I,* Interscience Publishers (New York—1951) at pages 321 and 348.

The unsaturated monocarboxylic acid moieties of the plant sterol monocarboxylic acid esters contain preferably 2 to 18 carbon atoms.

The most preferred plant sterol monocarboxylic acid ester additives are β-sitoesteryl acetate, β-sitosteryl oleate and stigmasteryl oleate.

Plant sterol monocarboxylic acid esters can be derived from free plant sterols by any convenient acylation method. For example, plant sterol monocarboxylic acid esters can be prepared by perchloric-acid-catalyzed esterifica-

tion of the free sterols with monocarboxylic acid anhydrides. Free plant sterols are readily commercially available.

As previously indicated, the level of added plant sterol monocarboxylic acid ester should be from 0.5% to 10% (free sterol equivalent) by weight, and preferably from 1.5% to 3% (free sterol equivalent), by weight of the total oil composition. The level of added ester must be at least 0.5% to provide significant hypocholesterolemic activity. The maximum amount of added plant sterol ester that can be utilized to provide a composition which gives maximum consumer satisfaction is that amount which is soluble in the oil at refrigerator temperature, that is at 40°F, i.e. an amount which is insufficient to come out of solution in the oil at refrigerator temperature. A 10% upper limit has been chosen herein as a practical upper limit and because when used in amounts in excess of that limit most plant sterol esters come out of solution in oil at refrigerator temperature. For example, an oil composition containing about 15% or more soy sterol caprate, as is disclosed in *J. of Nutrition 50*, 191—201 (1953), previously mentioned, is solid even at room temperature indicating insolubility of soy sterol caprate in oil in amounts greater than 10% (free sterol equivalent). Many of the plant sterol monocarboxylic acid ester additives of this invention are insoluble in oil compositions at refrigerator temperature at levels less than the above 10% upper limit. The solubility level depends on the carbon chain length of the monocarboxylic acid moiety and its degree of unsaturation. For example, acetates of plant sterols are only oil-soluble to the extent of 4% to 5% at refrigerator temperature while the corresponding oleates are oil soluble at refrigerator temperatures at levels greater than 10%. Most or all of the plant sterol monocarboxylic acid ester additives of this invention are soluble in oil at refrigerator temperature at and below the preferred upper limit of 3%.

In order to ensure the clarity of the compositions of this invention, the liquid glyceride base oil should preferably be substantially free of general purpose shortening emulsifiers such as mono- and diglyceride esters, lactylated glyceride esters, and any other materials which might tend to cloud the base oil or otherwise interfere with its clarity.

A wide variety of clear, liquid glyceride base oils can be used in the edible oil compositions (also called herein "cooking and salad oil" compositions) of this invention. Pure triglycerides liquid at refrigerator temperature, such as triolein, are suitable. Also included among suitable oils are the so-called natural salad oils, for example, olive oil, sunflower seed oil, safflower oil, and sesame seed oil. Other naturally-occurring liquid glyceride oils, for example, cotton-seed oil and corn oil are also useful; these oils are generally given a preliminary "winterizing", dewaxing, or similar treatment to remove the higher melting stearins before being used as a base oil. Certain other oils, for example, soybean oil, can be partially hydrogenated before use to improve their resistance to oxidative deterioration during prolonged storage periods; the higher melting solids formed during the hydrogenation treatment are preferably removed by winterization.

Suitable clear liquid glyceride base oils can also be obtained by directed, low temperature interesterification or rearrangement of animal or vegetable fatty materials, followed by the removal of the higher melting solids formed during the reaction. For an example of this procedure, see U.S. Patent 2,442,532. Another group of oils suitable for use as the liquid glyceride base oil is that group of oils in which one or more short-chain fatty acids, such as acetic acid and propionic acid, replace in part, the long-chain fatty acids present in natural triglyceride oils.

Other useful clear liquid glyceride oils can be derived from animal, vegetable and marine sources, and include mixtures of various such oils. Particularly preferred oils for use in this invention are triolein, cottonseed oil, soybean oil and mixtures thereof.

The cooking and salad oils of the invention can be conveniently prepared by dissolving liquid glyceride base oil and plant sterol monocarboxylic acid ester in a solvent and then evaporating the solvent. Suitable common solvents are any of the usual fat solvents, such as hexane or diethyl ether.

The cooking and salad oil compositions of the invention reduce the level of cholesterol in the blood that is directly of dietary origin up to 50% compared with the case when no hypocholesterolemic additives are utilized. The present compositions retain their efficacy even when utilized as an ingredient in other foods, for example in the production of bread.

The following example illustrates the present invention. All percentages in the example are by weight.

Example

Plant sterol monocarboxylic esters were dissolved in dietary triolein to make up clear cooking and salad oil compositions. Radioactive cholesterol was also dissolved in the oil compositions. The oil compositions were prepared by dissolving the radioactive cholesterol, plant sterol monocarboxylic acid esters, and triolein in diethyl ether and then removing the diethyl ether by evaporation. The resulting oil compositions contained, by weight, 1% cholesterol and the weight percentage sterol ester indicated in the Table below. The resulting oil was then emulsified with other dietary ingredients according to the following proportions:

Ingredient	Weight % of Total Diet
Sucrose	16.4
Vitamins in sucrose	3.6
Nonfat milk solids	18.2
Salt	1.8
Water	32.7
Cooking and Salad Oil	27.3
	100.0

Male rats (each weighing approximately 200 grams) that had been maintained on Purina Laboratory Chow ("Purina" is a registered trade mark) were fasted overnight and a cannula was inserted into their thoracic duct. Before closing the incision 10 millilitres of 0.9 percent NaCl in water was placed in the abdominal cavity. After recovering from anaesthesia, the animals were given 5 grams of the above proportions of dietary ingredients except that the diet included no cooking and salad oil ingredient. The rats were provided 0.9 weight percent NaCl in water for drinking.

On the following day about 5.5 millilitres of the above listed dietary ingredients (including the oil) were fed by stomach tube. Lymph was collected for 48 hours. Any animal whose lymph flow was less than 25 millilitres per 24 hours was discarded. The volume of lymph produced in 48 hours was determined. Duplicate samples of the diet and of the lymph were analyzed. The total amount of radioactivity in the lymph was used to determine the amount of dietary cholesterol that was absorbed. The reduction of dietary cholesterol in the lymph reflects the reduction of dietary cholesterol in the blood.

The sterol ester contents of the dietary oil, the cholesterol absorption results, and the percentage reduction in cholesterol absorption compared with a control are given in the following Table. In the Table, each result is an average result from the utilization of 10 rats.

TABLE

Plant Sterol Monocarboxylic Acid Ester	Level of Added Sterol Ester in Triolein Composition (Weight Percentage as Free Sterol Equivalent)	Dietary Cholesterol Absorbed (Percentage)	Dietary Cholesterol Absorbed in Control, i.e. With No Plant Sterol or Plant Sterol Ester Additive (Percentage)	Percentage Reduction in Dietary Cholesterol Absorption Compared with a Control
β-sitosteryl acetate[1]	2.0	40.8	58.5	30
	4.0	34.7	55.8	36
β-sitosteryl oleate[1]	2.0	45.2	56.8	20.4
	8.0	28.1	55.8	49
Stigmasteryl oleate[2]	2.0	45.6	56.8	19.8

[1]Acetate or oleate of plant sterol containing by weight 86.9% β-sitosterol, 8.9% campesterol, and the remainder impurity.

[2]Oleate of plant sterol containing by weight 87.6% stigmasterol. 7.6% β-sitosterol, 1.7% campesterol, and the remainder impurity.

The above Table indicates that cooking and salad oils having triolein as a clear liquid glyceride base oil and containing the levels of plant sterol ester indicated reduce cholesterol absorption from about 20% to about 50% compared with when control oil is used containing no plant sterol ester additive.

Cooking and salad oil compositions having triolein as a clear liquid glyceride base oil and containing the amounts of the particular plant sterol monocarboxylic acid esters indicated in the above Table are clear at room temperature, remain clear even at refrigerator temperature, and the sterol ester in them does not precipitate from the oil in the presence of water.

Cholesterol absorption reduction results similar to those above are achieved when refined and deodorized cottonseed oil or soybean oil hydrogenated to an iodine value of 107 is substituted for the triolein base oil above. These compositions are clear at room temperature, remain clear even at refrigerator temperature, and the sterol ester in them does not precipitate from the oil in the presence of water.

WHAT WE CLAIM IS:—

1. An edible oil composition comprising a liquid glyceride base oil and a plant sterol monocarboxylic acid ester in which the monocarboxylic acid moiety has from 1 to 12 carbon atoms of the carboxylic acid is saturated and up to 24 carbon atoms if the carboxylic acid is unsaturated, the said plant sterol ester being present in an amount of from 0.5% to 10% (free sterol equivalent) by weight of the composition, provided that the said plant sterol

ester is present in an amount such that it is substantially completely soluble in the base oil at 40°F.

2. An edible oil composition according to claim 1 comprising from 1.5% to 3% (free sterol equivalent) by weight of the total composition of the plant sterol ester.

3. An edible oil composition according to claim 1 or 2 wherein the base oil is triolein, soybean oil, cottonseed oil or a mixture of any of these.

4. An edible oil composition according to any preceding claim wherein the monocarboxylic acid moiety is unsaturated and contains from 2 to 18 carbon atoms.

5. An edible oil composition according to any preceding claim wherein the plant sterol ester has a plant sterol moiety derived from α-sitosterol, β-sitosterol, stigmasterol, ergosterol, campesterol or a mixture of any of these.

6. An edible oil composition according to any of claims 1 to 3 wherein the plant sterol ester is β-sitosteryl acetate.

7. An edible oil composition according to any of claims 1 to 3 wherein the plant sterol ester is β-sitosteryl oleate.

8. An edible oil composition according to any of claims 1 to 3 wherein the plant sterol ester is stigmasteryl oleate.

9. An edible oil composition according to claim 1 substantially as hereinbefore described in the Example.

10. A process for the preparation of edible oil compositions according to claim 1 which comprises forming a solution of the glyceride oil and the plant sterol ester and subsequently evaporating off the solvent.

11. A process according to claim 10 wherein the solvent is hexane or diethyl ether.

12. A process according to claim 10 substantially as hereinbefore described in the Example.

13. An edible oil composition whenever prepared by a process according to claim 10, 11 or 12.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.